

# Zinc Cementation – The Merrill Crowe Process

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## ABSTRACT

The classical method for the recovery of precious metals from cyanide leach solutions is cementation using zinc powder, the Merrill Crowe process, which was developed in the 1890's and used almost exclusively until the introduction of carbon adsorption processes in the 1970's and 1980's. The unit operations of the Merrill Crowe process include solid liquid separation, clarification, vacuum deaeration in packed towers, zinc addition and filtration of precipitated gold and silver using pressure filters. This paper discusses Merrill Crowe process application and circuit design including solution chemistry, preliminary process design parameters, equipment selection and sizing, process performance and relative costs.

## INTRODUCTION

Zinc cementation, which later became known as the Merrill Crowe Process, was the original method chosen for the recovery of precious metals from solutions generated by the cyanidation process, during its developmental stages. The zinc cementation process was first applied in the 1890's and was used, with subsequent improvements, until the introduction of carbon adsorption processes in the 1970's and 1980's. This paper discusses the application and design of the Merrill Crowe process beginning with a brief history of the process, the basic chemistry and the development of basic process design criteria for the development of a Merrill Crowe process flow sheet.

The Merrill Crowe process consists of the following main steps, which follow cyanide leaching:

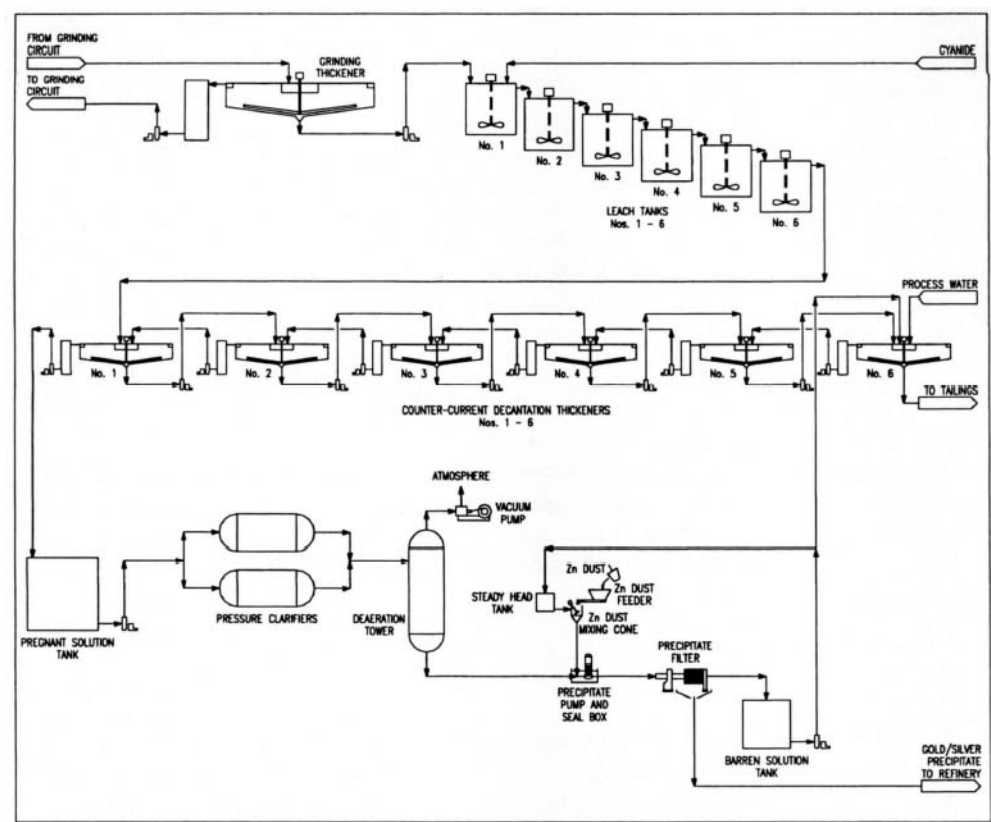
- Solid liquid separation, using CCD thickeners, or vacuum filtration;
- Clarification of pregnant solution to approximately 1 ppm suspended solids;
- De-aeration of the clarified solution using packed towers (Crowe) under vacuum;
- Addition of powdered zinc using a mixing cone;
- Precipitation in the pipeline between the press feed pumps and the filter presses;
- Filtration of the precipitated metals in a filter press;
- Smelting of the precious metal precipitate in the refinery to form dore;

Figure 1 is a simplified flow sheet of the Merrill Crowe process for low temperature cyanide leach solutions, requiring deaeration. A Merrill Crowe flow sheet designed to treat high temperature carbon elution streams, would be similar, but would not require the deaeration step (Marsden, 1990).

## History

Cyanidation was first applied in the extraction of gold and silver from low grade ores by J. S. McArthur and Doctors Robert and William Forrest of Scotland in the mid 1880's. A British patent

was issued to the group in 1887 and U.S. patents were issued in 1889 for the process, which included agitation of pulp in the presence of air followed by the precipitation of gold with zinc in a separate solution. The first mining application of cyanidation for gold recovery was at the Crown Mine in New Zealand in 1889. The process was subsequently applied in South Africa, the United States and mining districts around the world. The zinc cementation process was introduced in 1890 and became an integral part of the cyanidation process (Dorey, van Zyl and Keil, 1988; Fleming, 1998). The first application of the zinc cementation process in the United States was by C.W. Merrill at the Homestake Mine in Lead South Dakota in 1897 (Chi, 1992).



**Figure 1. Simplified flow sheet for a typical leaching, CCD and Merrill Crowe circuit.**

Zinc cementation was initially performed using long sloping boxes filled with bundles of coarse zinc shavings. Gold bearing solutions were passed through sand filters to remove suspended solids and then through the zinc boxes for metal precipitation. Vertical plates were installed in the boxes forming chambers to direct the flow of solutions through the beds of zinc shavings to improve the contact of the solutions with the zinc. The method proved to be effective but inefficient due to coating of the coarse zinc surfaces with deposited metals or insoluble zinc hydroxide. (Atwood, 1985; Wood, 1996)

Lead salts were introduced in 1894 to address the passivation problem. The bundles of zinc shavings were dipped in solutions of lead acetate before placement in the zinc boxes (Wood, 1996). The lead deposits on the zinc surfaces formed cathodic areas for preferential precipitation of precious metals, leaving the adjacent anodic zinc surfaces exposed for dissolution (Chi, 1992).

Clarification was found to be a very important stage, which affects both metal recovery and precipitate grade. When suspended solids were present, the rate of precipitation was found to decrease, which lowered recoveries. The zinc boxes acted as sand filters trapping fine materials that would potentially blind the beds of zinc and dilute the grade of the precious metal precipitate. (Atwood, 1985)

Through operating experience, it was also identified that some sands trapped in the zinc boxes, such as pyrite and marcasite, tended to improve precipitation and to lower zinc consumption. The improvement was attributed to the reaction of these sulfide minerals with oxygen and cyanide resulting in the consumption of dissolved oxygen. The reduced oxygen was found to improve the efficiency of the process by both reducing the passivation of the zinc surfaces and also by reducing the direct leaching of zinc, which requires oxygen (Atwood, 1985).

The next significant step in the development of the zinc precipitation process was substitution of zinc powder for zinc shavings in 1907-1908 by C.W. Merrill, while studying the effect of surface area on the rate of precipitation. Merrill added zinc dust (fume) to leach solution and then pumped the slurry through a filter press. The precipitate and zinc remained in the filter press and the barren solution was recycled to the process (Wood, 1996). The result was an increase in rate and recovery and improved zinc utilization. The increased surface area and reactivity also resulted in higher zinc consumptions as the rates of the passivation and zinc dissolution reactions increased, making it all the more important to remove oxygen from the system. In 1916, the vacuum deaeration tank was introduced by T.B. Crowe and incorporated into the Merrill Crowe process. (Atwood, 1985; Chi, 1992; Wood, 1996).

The Merrill Crowe process has generally remained in tact since 1916. The main improvements in the process since that time have been in the design and efficiency of the equipment and automation systems; clarifiers, vacuum towers with modern packing and filter presses. There is also a better understanding of the process chemistry, aiding in optimization of reagent usage and consumption resulting in reduced operating costs.

## **PROCESS SELECTION – CHOICE OF MERRILL CROWE VS CARBON ADSORPTION**

The two main processes currently in use for the recovery of precious metals from cyanide leach solutions are zinc precipitation and carbon adsorption. Fleming reports that the carbon in leach process has, in most cases, proved to be more efficient and to have 20 to 50 percent lower capital and operating costs than Merrill Crowe. Currently over 70 percent of world's gold production is recovered using carbon adsorption processes (Fleming, 1998).

The Merrill Crowe process has an advantage over the carbon adsorption process in cases where the metal concentrations are high, such as ores containing significant amounts of silver; high silver to gold ratios. Zinc cementation can also be applied to the recovery of precious metals from carbon strip solutions as an alternative to direct electrowinning.

Carbon in leach has the advantage over Merrill Crowe when ores contain significant levels of organic carbon, high base metal concentrations and when the ore contains high clays, which are difficult to filter.

Examples of operations, which utilize zinc cementation include:

- Newmont Mining Company - Minera Yanacocha mine in Peru
- Barrick Gold's Pierina Mine in the same district in Peru

- Placer Dome's La Coipa Mine in Chile
- Goldfields Operating Company, Chimney Creek- Carbon Strip Circuit
- FMC Paradise Peak – Carbon Strip Circuit
- Equity Silver Mine, British Columbia – Carbon Strip Circuit

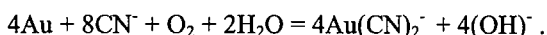
## PROCESS CHEMISTRY

### Cyanide Leaching

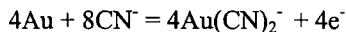
Leaching of precious metal ores in alkaline cyanide solutions yields metal bearing solution containing relatively low concentrations of gold, silver, copper, zinc, and other metal cyanide complexes depending on the composition of the ore and the type method of leaching employed.

The dissolution of gold and other metals in alkaline cyanide solutions is generally accepted to be an electrochemical reaction composed of two half-cell reactions. The oxidation of gold from  $\text{Au}^0$  to  $\text{Au}^+$  represents the most common anodic reaction. The cathodic half cell reaction consists of the reduction of oxygen and water. The reactions are corrosion type and occur in adjacent areas on the surfaces of gold particles. The gold (I) or aurocyanide complex is very stable and was reported by Finkelstein to be the predominant species formed in cyanide leach solutions. The stability of aurocyanide,  $\text{Au}(\text{CN})_2^-$ , is such that it remains stable in the absence of free cyanide and at very low pH. (Hedley, 1958; Finkelstein, 1972)

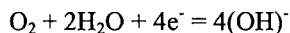
Gold is typically present in gold ores in elemental form or as an alloy with silver; electrum. The overall reaction for the dissolution of gold is represented by Eisner's equation (Hedley, 1958):



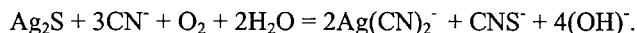
The anodic half reaction, the oxidation of gold, is represented by:



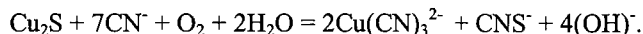
The cathodic half reaction, the reduction of oxygen and water, is represented by:



Cyanide soluble silver minerals, typically found in gold-silver ores, include electrum, an alloy of gold and silver, and argentite, a single sulfide mineral. More complex ores contain minerals such as tetrahedrite, which contain varying amounts of antimony and arsenic, can also be present. The overall reaction representing the dissolution of Argentite, silver sulfide, is represented by the following (Hedley, 1958):



The base metal reactions are of similar form. The dissolution reaction for chalcocite is as follows:



Some of the important metal complexes produced during the cyanide leaching of gold and silver ores include:

- $\text{Au}(\text{CN})_2^-$

- $\text{Ag}(\text{CN})_2^-$
- $\text{Hg}(\text{CN})_4^{2-}$
- $\text{Cu}(\text{CN})_3^{2-}$
- $\text{Zn}(\text{CN})_4^{2-}$
- $\text{Fe}(\text{CN})_6^{4-}$

Antimony and arsenic form soluble oxide compounds in alkaline solutions and are significant consumers of oxygen.

### Cementation Chemistry

The zinc cementation reaction in alkaline cyanide solutions is an electrochemical displacement reaction, which involves the reduction of gold and silver, which occur as cyanide complexes,  $\text{Au}(\text{CN})_2^-$  and  $\text{Ag}(\text{CN})_2^-$ , the reduction of oxygen and water and the oxidation and dissolution of the zinc metal which forms a cyanide complex,  $\text{Zn}(\text{CN})_4^{2-}$ . The gold and silver metal forms coatings on the surface of the zinc particles and the zinc in turn corrodes and dissolves into solution. The reactions are driven by the differences in electrochemical potential between the more noble precious metals and zinc. Metals, which are more electropositive than zinc, will reduced to their metallic states, while zinc will be dissolved. Table 1 contains a selection of reduction potentials for metals typically found in cyanide leach solutions.

**Table 1    Electrochemical Series – Standard Reduction Potentials (Vanysek, 1984, Finkelstein, 1972, Fang, 1992).**

| Reaction   | $E^0, \text{V}$ |
|--|-----------------|
| $2\text{H}^+ + 2\text{e}^- = \text{H}_2$                                 | 0.00            |
| $2\text{H}_2\text{O} + 2\text{e}^- = 2\text{OH}^- + \text{H}_2$          | -0.828          |
| $\text{Au}^+ + \text{e}^- = \text{Au}^0$                                 | 1.692           |
| $\text{Au}(\text{CN})_2^- + \text{e}^- = \text{Au}^0 + 2\text{CN}^-$     | -0.473          |
| $\text{Au}^{3+} + 3\text{e}^- = \text{Au}^0$                             | 1.498           |
| $\text{Ag}^+ + \text{e}^- = \text{Ag}^0$                                 | 0.8             |
| $\text{Ag}(\text{CN})_2^- + \text{e}^- = \text{Ag}^0 + 2\text{CN}^-$     | -0.269          |
| $\text{Cu}^+ + \text{e}^- = \text{Cu}^0$                                 | 0.521           |
| $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}^0$                             | 0.342           |
| $\text{Cu}^{2+} + 2\text{CN}^- + \text{e}^- = \text{Cu}(\text{CN})_2^-$  | 1.103           |
| $\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}^0$                             | -0.762          |
| $\text{Zn}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Zn}^0 + 4\text{CN}^-$ | -1.260          |
| $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$          | 0.401           |
| $\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}^0$                             | -0.126          |

The relationship between the change in Gibbs free energy,  $\Delta G^0$ , of an electrochemical reaction and the standard reduction potential,  $E^0$ , is represented by:

$$\Delta G^0 = - zFE^0,$$

where, z is the number of electrons transferred and F is the Faraday constant. To combine half cell reactions, the free energy for each reaction is determined and then summed. The free energy of the combined reactions can then be used to determine the new standard potential,

$$E^0 = - [\Delta G^0/zF].$$

The reaction will proceed spontaneously if the free energy is negative (Moore, 1983).

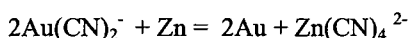
The cell potential for a system, which is not at unit activity, is determined using the Nernst equation,

$$E = E^0 + 2.303 RT/zF \log a_{\text{ox}}/a_{\text{red}}$$

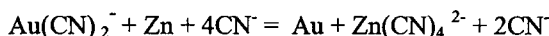
where E is the cell potential, R is the gas constant, T is the absolute temperature, z is the number of electrons transferred, F is the Faraday constant and  $a_{\text{ox}}$  and  $a_{\text{red}}$  are the activities of the oxidized and reduced species. The resulting cell potential is then used to calculate the change in Gibbs free energy for the reaction,

$$\Delta G = -zFE.$$

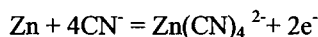
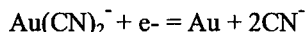
The reduction of gold by zinc metal is represented by the following overall reaction (Finkelstein, 1972),



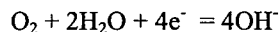
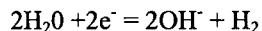
Assuming that free cyanide is available and a direct transfer of cyanide ions is not necessary (Marsden, 1990),



The half-cell reactions representing the reduction of gold and the oxidation of zinc are:

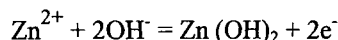
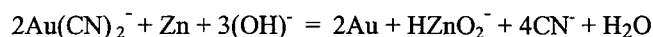
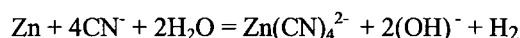
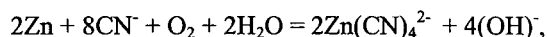


Water and dissolved oxygen are also reduced by zinc:



The efficiency of precious metal cementation is dependent on the effective dissolution of zinc, however if sufficient oxygen and free cyanide are available, zinc will dissolve independently, resulting only in increased zinc consumption. If the concentration of free cyanide becomes low, due to insufficient cyanide addition or excessive zinc addition, zinc will react to form zinc hydroxide, which may passivate zinc surfaces and plug filters.

Competing reactions include (Finkelstein, 1972; Fang, 1992):



Base metals including copper are precipitated along with the precious metals, though in practice it has been shown that copper precipitation can be minimized by maintaining an excess of free cyanide.

### Kinetics

The rate of the cementation reaction is first order with respect to the concentration of aurocyanide complex,  $\text{Au(CN)}_2^-$  and directly proportional to the surface area available for reaction as represented by the following equation (Finkelstein, 1972):

$$\log (C_0/C_i) = k A t$$

where:  $C_0$  = initial concentration of aurocyanide  
 $C_i$  = concentration of aurocyanide at time  $t$   
 $k$  = reaction rate constant  
 $A$  = zinc surface area available  
 $t$  = time

The rate is controlled by the diffusion of aurocyanide to the surface of the zinc particle under all conditions. The extent of reaction is limited by the amount of available cathodic surface. The anodic reaction is the limiting step only when the zinc surface is blocked by insoluble precipitate (Finkelstein, 1972).

### Effects of Operating Parameters on Zinc Precipitation

The zinc precipitation reactions are affected by the following parameters:

- pH
- $\text{CN}^-$  concentration
- Suspended solids concentration
- Dissolved oxygen
- Temperature
- Metal concentrations
- Lead addition
- Scale forming compounds such as calcium sulfate and sodium silicate

The effects of each of these parameters with respect to operating efficiency follow:

#### pH

- The pH must remain high to prevent the formation of volatile HCN gas.
- An increase in pH, in the absence of precious metal cyanide complexes, will tend to promote the formation of insoluble zinc hydroxide. (Finkelstein, 1972; Fang, 1992)

#### $\text{CN}^-$ Concentration

- The concentration of cyanide must be optimized along with the addition of zinc powder,
- Excess free cyanide will reduce the tendency for zinc hydroxide formation, but will lead to an increase in zinc consumption through independent zinc dissolution.
- Very low  $\text{CN}^-$  concentration results in the formation of  $\text{Zn(OH)}_2$  on zinc surfaces inhibiting cementation.

### Oxygen Concentration

- The rate of precipitation decreases with an increase in oxygen concentration;
- The rate of independent zinc dissolution reactions increases with an increase in oxygen concentration;
- The potential for redissolution of gold increases as the oxygen concentration increases and the zinc concentration decreases;

### Temperature

- An increase in solution temperature results in an increase in the rates of reaction for both precious metals precipitation and the dissolution of zinc, however the reactions are very fast at ambient temperatures;
- As the temperature increases, the solubility of oxygen decreases, which reduces the need for deaeration;
- Deaeration is not required when applying zinc precipitation to hot carbon strip solutions (Marsden, 1990);

### Zinc Concentration

- The amount of zinc required, to precipitate the precious metals, increases as the precious metal concentration decreases. The rate controlling step is the diffusion of metal cyanide complexes to the zinc surfaces (Finkelstein, 1972);
- Excess zinc addition must be optimized, as it will consume cyanide, which will allow formation of zinc hydroxide.

### Metal Concentrations

- The efficiency of cementation increases with an increase in metal concentration (Finkelstein, 1972);
- Base metals inhibit the precipitation of precious metals by forming coatings on the zinc particles;
- Base metals are large zinc consumers;
- Base metals precipitated in Merrill Crowe will have to be removed in the refining stage of the process.

### PbNO<sub>3</sub> Addition

- Lead nitrate additions of 10 to 15 parts per million increase the activity of zinc by forming a lead zinc couple. The lead precipitates on portions of the zinc surface forming cathodic areas and adjacent anodic zinc areas. Precious metals are preferentially precipitated on the cathodic lead surfaces and zinc dissolution occurs at the exposed zinc surfaces. Excessive lead addition will result in complete coating of the zinc surfaces, inhibiting cementation (Finkelstein, 1972; Chi, 1992; Fang, 1992);
- Lead increases the activity of zinc as described previously and reduces the tendency to form passivating layers of zinc hydroxide as cyanide concentrations decrease. If the cyanide concentrations fall too low, the lead will not prevent zinc hydroxide blinding (Fang, 1992);
- SEM work by Fang shows a change in the crystal structure of silver deposits on the zinc particles when lead is added. Without lead, a smooth coating of silver effectively covers



the surface of the zinc particles. With lead, the silver deposits form dendrites or clusters of crystals allowing contact of reagents with the zinc surface. Gold was found to form smooth deposits both with and without lead addition. (Fang, 1992);

#### Zinc Particle Size

- The rate of the cementation reactions increases with a decrease in zinc particle size.
- The rate of zinc dissolution increases as the zinc particle size decreases,
- Filtration becomes more difficult as the size of the zinc particle decreases.

#### Scale Formation

- Zinc dust will act as a seed particle for the precipitation of scale formers such as calcium sulfate and calcium carbonate, which will encapsulate the zinc particle.

### **CHARACTERISTICS OF COMMON CYANIDE LEACH SOLUTIONS**

Cyanidation is applied to a variety of ore types, which require different leaching methods and produce pregnant solution chemistries, which range from simple to very complex. The Merrill Crowe process can be applied to all of these systems, however there are those in which carbon adsorption, the chief competitor to Merrill Crowe, would prove to be more economic.

The most commonly used cyanide leaching systems include heap and vat leaching of coarse (greater than 8 mm) crushed ore, agitated tank leaching of finely ground (80 percent passing 74 microns) ore and flotation tailings, and agitated tank leaching of sulfide concentrates, which may be very finely ground (80 percent passing 45 microns). Zinc precipitation can also be applied to the recovery of metals from high temperature eluant from carbon stripping circuits (Marsden, 1990).

Solution characteristics for each system will differ due to the differences in grade, mineralogy, preparation and type of solid liquid separation applied. Solution quality will differ in suspended solids load, types of suspended solids, concentrations of precious and cyanide soluble base metals, solution temperature, free cyanide concentration, the presence of flocculants and scale forming compounds. Carbon, strip solutions are characterized by high temperature and high precious metal concentrations. Vacuum deaeration is not required (Marsden, 1990).

### **PROCESS DESCRIPTION AND DESIGN PARAMETERS**

This section provides a more detailed description of the Merrill Crowe process. The flow sheet assumed for the purpose of this paper is given in Figure 1, and example ranges of process design criteria are presented in Table 2. Development of actual process design criteria during engineering will require substantiation through metallurgical testing. Final equipment selection and sizing should be determined using the metallurgical test data and information from equipment manufacturers.

#### **Solid Liquid Separation**

Pregnant leach solution reporting from the solid liquid separation step will flow to a pregnant solution storage tank. The pregnant solution storage should provide sufficient volume to allow operation of the plant steadily and independently from the rest of the mill. The main issue will be scheduled and unscheduled mill down time. The pregnant solution storage tank also provides additional time for the settling of coarse solids which may carry over from the CCD or filtration sections. If flow is lost to the precipitate filters, the cake will be dropped and should be removed before restarting the plant to prevent blinding.

Table 2 – Merrill Crowe Process – Order of Magnitude Process Design Criteria

| DESCRIPTION                               | UNIT                             | VALUE/SPECIFICATION           | REFERENCE         |
|---|----------------------------------|-------------------------------|-------------------|
| <b>Solid Liquid Separation</b>            |                                  |                               |                   |
| Pregnant solution storage tank            | hrs                              | 4                             | Maintenance       |
| <b>Clarification</b>                      |                                  |                               |                   |
| Filter type                               |                                  | Horizontal pressure, US       |                   |
|   |                                  | Vertical pressure, Funda      |                   |
|   |                                  | Vertical tubular, Stellar     |                   |
| Specific solution flow rate               | m <sup>3</sup> /h/m <sup>2</sup> | 1.5 – 2.0                     | Atwood, 1985      |
| Number of filters                         |                                  | 2                             | Minimum           |
| Operating/Standby                         |                                  | 1/1                           |                   |
| Filter cloth type                         |                                  | Polypropylene                 |                   |
| Filter aid types                          |                                  | Diatomaceous earth or Perlite |                   |
| Suspended solids in feed                  | mg/L                             | 100 – 300                     |                   |
| Suspended solids discharge                | mg/L                             | 1                             |                   |
| <b>Deaeration</b>                         |                                  |                               |                   |
| Vessel types                              |                                  | Packed tower                  |                   |
| Packing types                             |                                  | Rings or tellerettes          |                   |
| Tower specific flow rate                  | m <sup>3</sup> /h/m <sup>2</sup> | 50 - 85                       | Atwood, 1985      |
|   | m <sup>3</sup> /h/m <sup>2</sup> | 70                            | Design            |
| Tower aspect ratio                        | ht to dia.                       | 2:1 – 3:1                     |                   |
| Vacuum required for deaeration            | mm Hg                            | 500                           |                   |
|   | Pa                               | 67,500                        |                   |
| O <sub>2</sub> conc. in pregnant solution | mg/m <sup>3</sup>                | 6                             | Varies w/ T and P |
| O <sub>2</sub> conc. in barren solution   | mg/m <sup>3</sup>                | 1                             | Design Target     |
| Precip filter feed pump type              |                                  | Vertical centrifugal          |                   |
| <b>Zinc Addition</b>                      |                                  |                               |                   |
| Zinc feeder type                          |                                  | Variable speed auger          |                   |
| Zinc addition rate                        | Stoichiometric                   |                               |                   |
| Gold                                      | g Zn/g Au                        | 0.33                          | Calculated        |
| Silver                                    | g Zn/g Ag                        | 0.61                          | Calculated        |
| Mercury                                   | g Zn/g Hg                        | 0.33                          | Calculated        |
| Copper                                    | g Zn/g Cu                        | 1.03                          | Calculated        |
| Excess zinc addition rate                 | Typical                          | 150 – 300%                    | Design            |
| <b>Metal Concentration vs. Excess</b>     |                                  |                               |                   |
| 100 ppm                                   |                                  | 10%                           | Atwood, 1985      |
| 5 ppm                                     |                                  | 200%                          | Atwood, 1985      |
| 1 ppm                                     |                                  | 1,500%                        | Atwood, 1985      |
| <b>Zinc induction</b>                     |                                  |                               |                   |
| Very high grade solution                  | 200–300ppm                       | Agitated mixing cone          |                   |
|   |                                  | Dry zinc to reaction tank     | Mansanti, 1989    |
| Lead nitrate addition                     | ppm                              | 10 – 15                       | Fang, 1990        |
| <b>Precipitate Filter</b>                 |                                  |                               |                   |
| Type                                      |                                  | Plate and Frame               |                   |
|   |                                  | Horizontal leaf (Funda)       |                   |
|   |                                  | Tubular (Stellar)             |                   |
| Specific Flow Rate                        | m <sup>3</sup> /h/m <sup>2</sup> | 4.5                           | Typical           |
| Operating cycle time                      | days                             | 7                             | Typical           |
| <b>Precipitate Composition</b>            |                                  |                               |                   |
|   |                                  |                               | Ore Dependent     |
| Gold + Silver                             | %                                | 30 – 80                       |                   |
| Zinc                                      | %                                | 5 – 30                        |                   |
| Lead                                      | %                                | 0.2 – 2                       |                   |
| Copper                                    | %                                | 0.1 – 2                       |                   |
| Mercury                                   | %                                | 0 – 2                         |                   |
| Insol                                     | %                                | 5 – 15                        |                   |
| Barren Set Point                          | g Au/t                           | 1.7                           | Mansanti, 1989    |

## **Clarification**

The pregnant solution, typically thickener overflow solution will be pumped from the pregnant solution storage tank through pressure filters, to reduce the solids concentration from a typical 100 to 300 part per million range to less than 1 part per million. Clarification is achieved by the use of pressure filters containing either horizontal or vertical leaves, which can be automatically washed. At least two pressure filters should be available which can be operated in parallel with one operating and one on standby to allow continued operation through wash cycles.

The pressure filters consist of horizontal tanks, which contain a series of filter disks mounted on the solution discharge pipe, which extends through the center of the tank. The filter elements or disks are covered with a polypropylene cloth, which is must be precoated with a layer of fine silica to create a bed of filter media to trap very fine particles. The fine silica consists of either diatomaceous earth or perlite and can be purchased with varying particle size distributions. The blend of precoat materials used for a given operation is selected to provide the required solution clarity, the highest flow rate, lowest pressure drop and longest filtration life. The optimization of these variables will be unique to each operation and procedures will be developed based upon each specific ore type. In addition to precoating the filters, a continuous addition of the diatomaceous earth may be added directly to the pregnant solution as body feed, when the suspended solids are very fine or clay rich.

Pregnant solution is pumped through the pressure filters until the pressure drop increases to a preset limit based on the pressure rating of the filter and the flow rate through the filter, which will decrease as the pressure increases.

At the end of the filtration cycle, a second parallel filter is placed on line to maintain the desired process flow rate, and the filter to be cleaned is taken off-line. The filter tank is drained along with filtered solids that will slump by gravity from the filter clothes when the process solution flow is discontinued. The filter cloths are then washed with built in high pressure sprays which remove filter cake that may stick to the cloths. The filter discs rotate past the sprays. Upon completion of the wash cycle, the vessels are closed and filled with barren solution and the precoating process is initiated.

The precoat system consists of a precoat mix tank and circulation pumps. The appropriate amount of precoat is added to the precoat mix tank and the precoat slurry is then circulated in a closed loop through the filter vessel until the returning solution becomes clear. The filter is then put back into operation by introducing pregnant solution while closing the precoat circuit, being careful to maintain differential pressure on the filters so that the layer of precoat will remain in place. If differential pressure is lost across the filter the precoat will fall to the bottom of the vessel and the process must be repeated.

The sizing of the filters is based on the flow rate of pregnant solution and the amount and type of suspended solids contained in the solution. Typically the filters are designed for a specific flow rate in the range of 1.5 cubic meters per hour per square meter of filter area.

Blinding of the filter cloth is the leading problem, which affects the performance of the clarification filters and may determine the ultimate cycle time. Some of the sources of blinding include:

- Flocculent from the CCD circuit;
- Very fine suspended solids; clays;
- Calcium carbonate precipitation or scaling can cause premature blinding of filters. Antiscalants are used to prevent the scaling problem.

- Precipitation of sodium silicate gel on the filters can be a problem if significant amounts of sodium hydroxide are used in the leaching circuit. Potential sources of sodium hydroxide in the leaching circuit include cyanide addition, especially when using low concentration, recovered cyanide, and final pH control.
- Precipitation of iron hydroxides.

### Deaeration – Crowe Tower

Deaeration of the clarified pregnant solution is typically accomplished using a packed tower under vacuum. Clarified pregnant solution discharging the filters flows to the top of the deaeration tower, where the solution is distributed over a bed of packing, which provides surface area for thin film formation and release of dissolved oxygen. A vacuum pump is used to reduce the pressure within the vessel to approximately 500 mm Hg or 67,500 Pa. Evolved gases including oxygen and ammonia are exhausted through the vacuum pump. Deaerated solution discharges from the tower, by gravity, through a vertical discharge pipe directly into the suctions of the product filter press feed pumps. The height of the discharge pipe, which remains full of solution (the barometric leg), is determined by the amount of head required to overcome the vacuum developed by the vacuum pump and to provide the required net positive suction head for the filter press feed pumps.

Various types of towers have been used for deaeration, from the original Crowe tower, which contained triangular section, wooden boards, to modern packed towers that use efficient polypropylene rings, saddles or tellerettes. In addition to packed towers, bubble cap tray or baffle towers could be used. Baffle towers consist of plate arrangements within the towers. The solution will cascade over the edge of one plate to the next forming a thin curtain of droplets providing surface area for transfer. Baffle tower arrangements include the disk and donut type and opposing inclined plate. The advantage of baffle towers is that they are less susceptible to blockage by carbonate or gypsum scale than the more efficient dumped packing (Fair, J.R., 1984).

In sizing a packed tower, the diameter is determined by the liquid flow rate, the capacity of the packing and the gas flow rate, which moves countercurrent to the solution. These rates along with the characteristics of the liquid and gas streams can then be used to estimate the pressure drop and predicted flooding points for a packed tower using the pressure drop correlation by Eckert (Fair, J.R., 1984). The pressure drop correlation helps to define the acceptable operating range of a tower and provides a means to optimize the tower diameter.

The height of the packing within a tower can be determined from the overall volumetric liquid phase mass transfer coefficient,  $K_La$ , for the process, which is found experimentally (Edwards, W.M., 1984). The relationship between the mass transfer coefficient and the packing height is given by the equation:

$$K_La = n_A / (h_T S \Delta x^*_{lm}),$$

where  $n_A$  is the overall rate of transfer of solute A,  $h_T$  is the total packed depth in the tower,  $S$  is the tower cross sectional area, and  $\Delta x^*_{lm}$  is the log mean concentration difference given by:

$$\Delta x^*_{lm} = (x^* - x)_2 - (x^* - x)_1 / \ln[(x^* - x)_2 / (x^* - x)_1]$$

where subscripts 1 and 2 designate the bottom and top of the tower respectively.  $x^*$  is the mole fraction of gas in the solution which is in equilibrium with the bulk gas concentration, and  $x$  is the mole fraction of gas in solution (Edwards, W.M., 1984).

The equilibrium gas concentration in the solution at the specified pressure can be determined using Henry's Law,

$$p_A = Hx_A ,$$

where  $H$  is the Henry's law constant,  $p_A$  is the partial pressure of  $A$  in the gas phase and  $x_A$  is the mole fraction of  $A$  in solution. If  $A$  is assumed to be air and  $p_A$  is the total pressure, the concentration of oxygen can be estimated from the chemical composition of air (Edwards, W.M., 1984).

The desorption of oxygen, hydrogen and carbon dioxide from water was studied by Sherwood and Holloway and correlations were developed for the mass transfer coefficient and the height of a transfer unit for the system. The correlations can be used along with the generalized equation by Cornell to determine the packing height for various types of packing (Fair, J.R., 1984).

The best source for mass transfer data including the overall mass transfer coefficient would be from existing commercial operations. Performance data on various packing types and materials can be obtained from the packing and tower internals manufacturers.

The specific flow rate for preliminary design of packed, vacuum, deaeration towers is approximately  $70$  to  $85 \text{ m}^3/\text{h}/\text{m}^2$ . The height to diameter ratio for reported towers ranges from  $1:1$  to  $3:1$ . The  $3:1$  ratio is more common and is thought to be more efficient as long as the tower is not allowed to operate in a flooded condition. The vacuum pump is sized for the maximum amount of gas to be transferred and the target absolute pressure of  $67.5 \text{ kPa}$ .

## Cementation

Zinc powder is metered into the deaerated pregnant solution using various types of feeders. Some commonly used feeders include, variable speed auger type feeders and rotating disk. In most cases it is necessary to use a vibrating feed hopper to prevent bridging.

Zinc powder is typically fed into a small agitated mixing cone containing barren solution, which is positioned above the suction of the filter press feed pumps. The zinc slurry will flow by gravity, through a control valve, into the pump suction. The zinc cone should be installed on a platform adjacent to the deaeration tower and above the liquid level in the tower to allow gravity flow into the pump and prevent overflowing when the filter press, feed pumps are shut down. A steady head tank will be provided to maintain a constant level in the mixing cone.

The zinc addition rate will be the stoichiometric amount of zinc required to precipitate the precious and base metals in solution plus an excess amount, which will be dependent on the metal concentrations of the solution. The excess zinc required with respect to metal concentration in solution has been reported to be ten percent for solutions containing 100 parts per million metal, 200 percent for solutions containing 5 parts per million metal and 1500 percent for solutions containing 1 part per million metal (Atwood, 1985). (Marsden, 1991) reported that five to 10 times the stoichiometric requirement would be needed for carbon eluants.

The cementation reaction occurs very rapidly and sufficient retention time is available for the reaction to take place in the pipeline between the filter press feed pumps and the filter presses. The key issue in the design of the filter press feed pumps is the prevention of air ingress. Leakage of air through the pump shaft seal will allow oxygen to enter the system. The standard method of coping with this problem is to use inline vertical centrifugal pumps, which are submerged in barren solution above the shaft seal.

Operating problems reported in adding zinc slurry to the system include wetting of the zinc, control of the zinc solution feed rate, plating of metals on the wetted parts of pumps and build-up of zinc and precipitate in the pumps and pipelines. Extreme cases are reported in the treatment of

very high grade carbon strip solutions (Mansanti, 1989). In the Chimney Creek case, the plating and build-up problem lead to the addition of a separate pumping system to inject the zinc slurry into the press feed pump discharge line. One recommendation to minimize the plating problem or at least contain it was to add dry zinc to an agitated reaction tank to permit the precipitation reaction to occur before entering the piping system (Mansanti, 1989).

### **Precipitate Filtration**

Filtration of the precipitate has been accomplished in various types of pressure filters. A common type is the plate and frame filter press. Others include enclosed, automated, horizontal leaf filters and candle or tubular type filters. Plate and frame filter presses can be fitted with canvas or polypropylene filter clothes. In some cases a combination of canvas filter clothes covered by filter paper has been used. The filter presses are typically precoated with diatomaceous earth or perlite at the beginning of the filtration cycle to prevent blinding. Zinc can be added along with the precoat to insure that the gold is completely precipitated during the start-up of the precipitation/filtration cycle. During steady state operation, the presses will contain excess zinc.

The filters will be operated for specified periods of time determined by the maintenance schedule, the accounting schedule, the time it takes for the pressure to reach the maximum recommended operating level or the flows decrease to an unacceptable level. At the end of the selected operating cycle, the filters are taken off line and drained. Compressed air is blown through the filters to force as much of the liquid out of the filter cake as possible. The presses are then opened and the filter cake is dropped into carts, which can be transported to the refinery. This operation is sensitive to security and is typically performed under the supervision of the refinery personal and plant security staff.

The filter clothes are scraped and washed, the presses are reassembled and the system is put back in operation. The precipitate is then transported in the same cart to the refinery area for smelting.

### **Clean-up and Smelting**

There are different approaches to the treatment of Merrill Crowe precipitates in the refinery depending on the composition of the precipitate and the types of equipment available. The three main types of furnaces referred to in the literature include gas or diesel fired reverberatory, submerged arc and induction type furnaces. Induction furnaces are typically not the best choice for the smelting of zinc precipitate unless the precipitate is acid washed prior to smelting. Induction furnaces only heat the metal and so the slag is heated indirectly. The high quantities of fluxes result in reduced crucible life. The reverberatory furnace has been used successfully in operations requiring high flux to charge ratios. The reverberatory furnace is either gas or diesel fired and provides heating directly to the top of the melt allowing the use of higher temperature slag mixtures.

The precipitate clean-up and smelting processes at the Nerco DeLamar Mine and at Coeur Rochester were similar. The precipitate at DeLamar in the late 1980s and early 1990's was filtered using plate and frame filter presses. The filter cloths were covered by filter papers, which were removed along with the precipitate during cleanup. The wet precipitate was mixed with fluxes and loaded into the 2000 lb copper reverberatory furnace. The smelting process was performed in a single step and dore bars were poured. It should be noted that the precipitate at DeLamar was relatively free of base metals.

Treatment at the Rand refinery was much more involved. The precipitate was washed from the Stellar filters into vats in which sulfuric acid was introduced to dissolve the zinc. After acid washing, the remaining gold leach residue was filtered using plate and frame, drum or belt filters

and the filter cake was packed into calcining trays. The residue was calcined at a temperature ranging from 550 to 700 degrees C for 16 hours. The resulting calcine was then smelted in submerged arc furnaces.

The treatment process at Paradise Peak included an initial sulfuric acid leach step followed by filtration and retorting of the filter cake in order to remove and capture the mercury. The retorting process was performed over 24 hour period at a temperature of 730 degrees C (1350 F) (Mansanti, 1989).

Equity Silver acid leached the precipitate using hydrochloric acid. The residue was filtered, drying and fired in a 225kg induction furnace. The buttons from the first pour were then remelted in a 45 kg induction furnace. Initially, sulfuric acid was used to leach the precipitate, however, sulfates and sulfides remaining in the leached residue resulted in the formation of significant sulfide matte layers during melting (Semple, 1987).

## **OPERATING COST VARIABLES**

### **Consumables**

The operating costs associated with the Merrill Crowe process are associated with operating and maintenance labor and consumable items. The preliminary design criteria presented in Table 2, include estimated unit consumptions for some of the consumable items. The following is a summary of the key operating costs

### **Manpower**

Operating Labor  
Maintenance Labor

### **Consumables**

|              |                        |
|--------------|------------------------|
| Power        | Zinc                   |
| Cyanide      | Lead nitrate           |
| Filter aid   | Antiscalant            |
| Filter cloth | Filter paper (if used) |
| Propane      | Freight                |

Actual operating costs for a given project should be estimated based on the results of metallurgical test work, local labor costs, local power and quotes for all consumables including freight. In very remote regions, the availability of operating and maintenance supplies may dictate the type of plant constructed.

## **CONCLUSIONS**

The zinc precipitation or Merrill Crowe process has proved to be a flexible, time tested method for the recovery of precious metals from cyanide leach solutions and can be applied to the majority of ore types except those containing organic carbon. The key parameters for the successful operation of zinc precipitation include:

- Low concentrations of suspended solids
- Low concentrations of dissolved oxygen
- Low base metal concentrations
- Optimized free cyanide concentration during precipitation
- Optimized zinc addition rate
- 10 to 15 ppm lead nitrate addition

The carbon adsorption processes have steadily improved over the last twenty years and are now reported to be more efficient and less costly than zinc precipitation for many applications. Cases in which zinc precipitation remains more cost effective than carbon adsorption include the treatment of ores containing high silver to gold ratios and ores containing significant mercury concentrations. Carbon adsorption is required for processing ores containing organic carbon and carbon adsorption has an advantage over zinc precipitation when high base metal concentrations are present and where high clay is present preventing effective solid liquid separation.

To obtain the benefits of both processes when treating high silver ores, operators have applied a combination of Merrill Crowe and carbon in leach. Initial pregnant solution or No. 1 thickener overflow solution is treated in a Merrill Crowe circuit to remove the majority of the silver and the thickener underflow and remainder of the slurries and solutions are treated using either carbon in pulp or carbon in leach processes.

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